

Development of Biodegradable polymers

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Additionally we emphasize the biological degradability of polyolefins, produced by TVK PLC.

In the experimental part we describe a method in case of a chosen polypropylene type, whereby the initialization of the polyolefin's degradation process is obtainable and methods to control, monitor the process. The examinations partly were made by Nor-X Industry AS Norway Company who contributed to the execution of the experiments by their products and equipments.

Abstract

In the last few decades plastic production increased rapidly all over the world, and because of this also the plastic waste in the environment is getting higher and higher, resulting more environmental load. The case is especially serious in the field of packaging materials. If we would be able to develop modified base materials in these areas, which are biologically degradable, we could decrease the negative effect to the environment significantly. We can get such materials in two ways: on the one hand we can produce 100% degradable plastics; on the other hand we can modify traditional polymers with special additives to become degradable.

In our article we overview a survey of the effects of synthetic plastics' on the environment, and on their recycling possibilities. We describe the bases of the biological degradation and the main types of degradable polymers.

Összefoglalás

A jövő műanyaga a környezetért – biológiailag lebomló műanyagok előállításának lehetőségei

A világon a műanyagtermelés az utóbbi évtizedekben óriási szintre nőtt, ezért egyre nagyobb mennyiségben kerülnek ki a környezetbe műanyag hulladékok, amelyek jelentős mértékben növelik annak szennyezettségét. Ez leginkább a csomagolóanyagok területére igaz. Amennyiben ezen a területen képesek lennének olyan módosított alapanyagokat kifejleszteni, melyek biológiai úton lebomlóak lennének, azzal jelentős mértékben hozzá tudnánk járulni a környezeti terhelés csökkentéséhez. Ilyen alapanyagokat két úton kaphatunk: egyrészt eleve 100 %-ban lebomló műanyagokat gyártunk, másrészt a hagyományos polimereket bizonyos adalékanyagokkal lebomlóvá tesszük.

Cikkünkben elméleti áttekintést adunk a szintetikus polimerek környezetre

vetített hatásairól, újrahasznosítási lehetőségeiről. Bemutatjuk a biológiai degradáció alapjait és a lebomló polimerek főbb típusait. Külön kitérünk az általunk is gyártott poliolefinok biológiai lebonthatóságára.

A kísérleti részben egy kiválasztott polipropilén típuson keresztül bemutatjuk azt a módszert, amivel elérhető a poliolefin hulladékok degradációs folyamatának inicializálása és azt a vizsgálati módszert, amivel ezt nyomon követhetjük. Vizsgálatainkat a Nor-X Industry AS norvég céggel közösen végeztük, akik termékeikkel és készülékeikkel hozzájárultak a kísérletek kivitelezéséhez.

Introduction

Man has known and used various natural polymers (e.g. resins, caoutchouc) since ancient times. The modification of these natural polymers started up the mass production of the first plastics as early as in the 19th century (rubber, nitrocellulose); however it was not earlier than the beginning of the last century when the nature of macromolecules became known. This triggered a rapid development in the world's plastic industries where new plastic types are invented and put into mass production every day, beginning with the production of phenol resins and synthetic caoutchouc through today's commodity plastics (low and high density polyethylene, polypropylene, PVC, etc.). Plastics production has reached huge quantities in recent decades worldwide. Between 2002 and 2006, plastics production increased by 45 million tons (to 245 million tons from 200 million tons). This quantity includes the yearly consumption of thermoplastics of which increased to 197 million tons in 2006 from 152 million tons consumed in 2000, and according to latest forecasts, this

consumption quantity will certainly reach 250 million tons by 2010 [1, 2].

It is more than obvious that neither the manufacturing, nor processing or consumption of plastics can be addressed without their environmental implications. It is easy to understand that the huge production and consumption capacities mentioned earlier cause an ever increasing environmental load when plastic products land in the environment as wastes at the end of their life cycles. This is especially true in the case of plastic packaging materials (for polyolefins in particular), since in Europe alone 35-40% of plastic products are used in this field of application [3].

In recent years, more and more research focuses on biodegradable polymers or on the modification of traditional, normally not biodegradable plastics in order to make them biodegradable. This article briefly discusses this field of chemical research.

Theoretical overview

THE IMPACTS OF SYNTHETIC POLYMERS ON THE ENVIRONMENT

Relatively few polymers end their life paths as unrecoverable wastes. In most developed countries, household garbage including plastic wastes will be deposited in dumpsites or burned in incinerators. Burying the wastes in the soil is becoming a less accepted practice of waste treatment, because in anaerobic circumstances wastes tend to generate methane, a gas, which has a much higher greenhouse effect than carbon dioxide does. In some cases, methane released during the decomposition of plastic wastes has caused explosions. Figure 1 outlines some preferred ways of waste recovery [4].

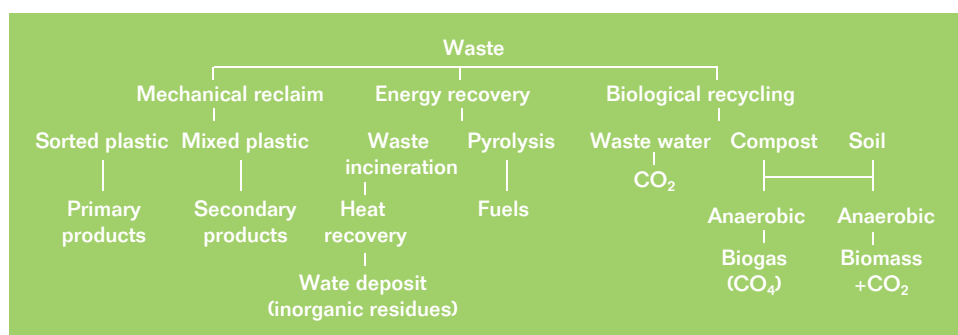


Figure 1. Recycling options for polymer wastes [4]

At the first glance, the incineration of wastes looks a favourable option to recover the high heating value of carbon based polymers. However, there is a wide public distrust of incinerators primarily because of their possible toxic emissions. PVC is considered number one of the potential hazard sources, because it may release dioxin while burned. Notwithstanding these concerns, the recovery of the energy trapped in plastic wastes will be a more and more required option of waste treatment in the future. Generally speaking, by reclaiming plastic wastes mechanically we can produce simple products. This process is less feasible for the recycling of mixed plastic wastes, whose pyrolysis will still remain an option to produce fuels, petrochemical products, or monomers in some cases. We know that biodegradation channels natural wastes back to carbon circulation, a process, which produces biomass as a primary product, which allows the new generations of vegetation to germinate in. It is also known that the formation of biomass binds carbons contained in the waste for much longer than the burning of the same waste normally does, and therefore, biomass generation poses less burden to the atmosphere. There are two categories of biodegradable polymers. One is where biodegradability is an inherent property of the products. One example of inherently biodegradable plastics is medicine capsules where a precisely controlled degradation has a decisive role to release the effective component at a specific point of the alimentary canal. Other inherently biodegradable plastics are the polyethylene films used in horticulture, which allow earlier sowing and prevent fewer weeds from emerging. The second category comprises most environment-friendly packaging materials, primarily, including the convenient polyolefins, which can be turned into compost by aerobic oxidative biodegradation.

THE BASICS OF BIODEGRADATION AND THE MAIN TYPES OF BIODEGRADABLE PLASTICS

Biodegradation is the capacity of micro organisms to influence abiotic degradation through a series of physical, chemical and enzyme effects. The interactions taking place between biological degradation and various environmental effects act as very important factors in this process. Heat, mechanical stresses, oxygen, contaminants and water are the most important players in the process. The presence of water is indispensable for the micro organisms to play their roles. Particle size and surface area, too, have to be

mentioned as further important ingredients, because biodegradation takes place on the surfaces of the polymers to the most part. In certain applications, including especially packaging and farming, the products have limited service lives, often not longer than only a few weeks or months. In these applications it would be most favourable if natural external effects could cause the products no longer needed to decompose either on the site of their use, or on waste deposits, or on other designated areas. Among the products with limited or controlled life cycles the soil cover films, garbage bags, certain bottles and drums, disposable fast food items (cups, trays and cutlery), and containers are the most important.

Looking at today's research, we can identify two well differentiated areas. One focuses on specialty polyesters which are genuinely, or 100% degradable, and the second one addresses more traditional types of plastics which contain additives, including starch or organic metal compounds as modifiers intended to make these products degradable. The first path of research starts from the fact that the product is inherently degradable and studies the areas where these plastics can be reused. The other one goes in the opposite direction and seeks to find ways to modify the basic materials of plastic products used in specific applications in order to make them biodegradable.

POLYESTER TYPE BIOPOLYMERS

The fully degradable polymers like these specialty polyesters have now been in the centre of research for about 15 years, however only a modest commercial success has been produced, so far. At present, the only high capacity commercial unit being in service in the world (Cargill and Dow) produces 140 Kt PLA in a year, and there are a number of lower capacity plants in various countries, e.g. in Belgium, too (Total Petrochemicals and Galactec Escanaffles) where the production goes up to 1.5 Kt per year [5].

This type obviously comprises a number of subtypes (depending upon the nature of the product: natural, partly synthetic, or fully synthetic), which are indicated in the following table, giving their acronyms, as well.

We can state that aliphatic polyesters, whose yearly production quantities remain below those of polyolefins, are expensive, sensitive to hydrolysis, their production is problematic, and

AAC	Aliphatic-aromatic copolyester
PBAT	Polybutylene adipate/terephthalate
PBS	Polybutylene succinate
PBSA	Polybutylene succinate/adipate
PCL	Polycaprolactone
M-PET	Modified polyester
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHE	Polyhydroxyethanoate
PHBV	Polyhydroxybutyrate/valerate
PLA	Poly(lactic acid)
PTMAT	Polymethylene adipate/terephthalate

1. Table Polyester type biopolymers [5]

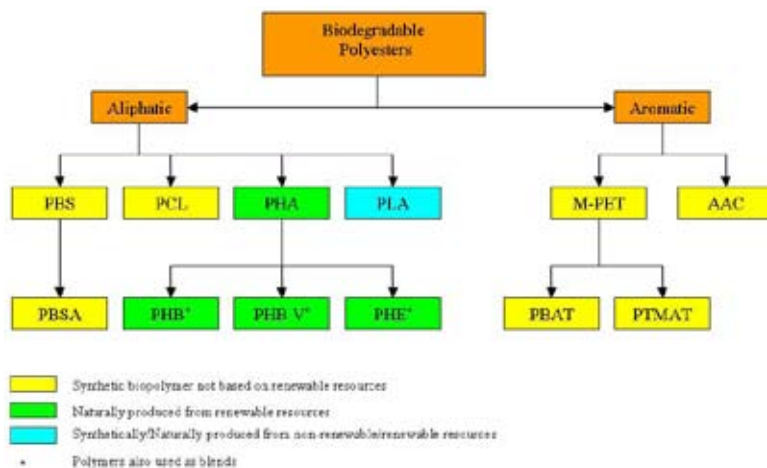


Figure 2. Groups of biodegradable polyesters [5]

have low thermal stability and poor mechanical properties, moreover, they can change in time. The cheapest of them is the synthetic based PCL. PHB is synthesized by bacteria, which accumulate it as a spare nutrient in their organisms. PLA is generated from maize starch by fermentation and used to make disposable cutlery, which will fully decompose in the environment.

The properties of normal polylactic acid are much similar to those of polystyrene. It is resistant to water, though not resistant to high temperatures (>55°C). Because it is rigid and stiff, it is necessary to use plasticizers to improve its properties. Its sealing capacity is poorer than that of PET, but well compares to that of PP. The main advantage of this plastic is that it rapidly decomposes even in the lack of light.



Figure 3. PLA cutlery

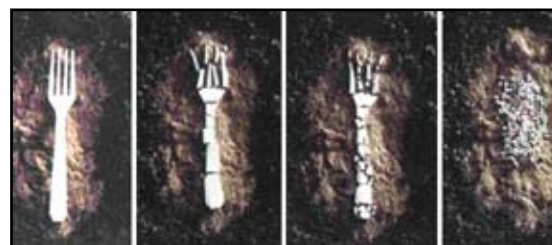


Figure 4. The stages of the degradation of a fork on day 0, 12, 33, 45

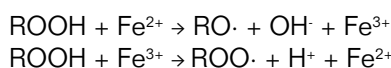
Notwithstanding experience showing that aromatic esters cannot be degraded, attempts have been made to copolymerise higher mechanical property aromatic polyesters with aliphatic polyesters in order to develop products that may as well be biodegradable.

BIODEGRADABILITY OF POLYOLEFINS

Generally speaking, thermoplastics are synthetic polymers, whose structure is built of carbon bonds which are highly resistant to microbiological effects. However, it has recently become known that certain micro organisms can use low carbon polyolefins as nutrients, provided their molecular

mass is not higher than 500 g/mol [6]. Even so, the biodegradation of polyethylene still remains a slow process. Corbin and Henman studied the degradation of ^{14}C -marked polyethylene and found its yearly conversion rate not higher than 2% [7]. The reason for this may be that the terminal methyl groups in the polyethylene can oxidize to carboxylic acids primarily, while β -oxidation goes on by stages.

One precondition of biodegradation is photo degradation and/or chemical degradation. In general, polyolefins are known to be highly resistant to degradation, partly because of their hydrophobic nature, which prevents hydrolysis, and partly because of the commonly applied antioxidant additives in them, and also because of their very high molecular masses [8]. In order to make polyolefins degradable, additives are needed to allow photo degradation and chemical degradation to take place and produce segments in the plastic whose molecular masses are lower than 500g/mol, which can be then degraded by micro organisms. Of these additives (aromatic ketons, aromatic amines, and organic compounds of transient metals) the metal salts or metal complexes where the metals can change their oxidation stages are found to give the best systems [9]. The most commonly used additives are cobalt, cerium and iron or their fat soluble compounds. Iron stearate is preferred to other members of this additive family, because plastics containing this additive are harmless to the environment and more compliant with food standards than plastics with other transient metal additives are. The main point of the process is that the iron ions contained in the additive make a catalytic effect on the oxidative degradation of polyolefins, a process, which is initiated by light and/or heat. The following most important reactions take place:



The hydroperoxides in the above reactions are generated during the oxidative degradation of polyolefins, and by accelerating their decomposition we can speed up the rate of degradation, as well. The disadvantage is that in ambient conditions iron(II) and iron(III) ions are tend to be precipitated in the forms of insoluble iron-oxide or iron-sulphate, which slows down the process of degradation. A further disadvantage is that the rate of degradation may slow down also when these plastics get into the soil or compost.

Starch is commonly added to polyolefins to help their degradation. In natural conditions however

and when no prooxidants are present, starch will be used up and simply run out before the actual degradation of polyolefins commences. Blends containing starch have a continuous starch phase, which can be easily digested by the α and β amylase enzymes of micro organisms. After the continuous phase disappears a porous polyolefin and starch blend is left behind. In case also prooxidants are present, the degradation of the polyolefin matrix will take place at a faster pace [10-11].

It is a natural expectation that the macromolecules of biodegradable plastics should get fragmented quickly in order to cause a full biodegradation of these plastics when they get to the end of their life cycles [12]. Above to reach full degradation however, it is also important that the mechanical properties of these plastics do not change significantly during the application of the products, that is, they should have a controlled service life, so that these plastics can meet the requirements of both degradability and application.

Experimental part

The plants in Tiszaújváros and in Bratislava of the Petchem Division produced more than 1.2 million tons of polymer products in 2007, most part of which was used in the packaging industry according to world trends. A great many of these packaging materials (bags and packaging films) have short useful lives and turn into wastes as soon as the products (e.g. food) they wrap are used up. In order to reduce the environmental impacts of our products, we find that the second path of research, focusing on making traditional polyolefin products biodegradable by modifying them is the most feasible option for us.

TVK PLC first decided to study this field on the initiative of a Norwegian company, Nor-X Industry AS. This company prepares specialty masterbatches (pellets containing higher quantities of some additives for the purpose of making the processing simpler) intended to help the degradation of polyolefins. TVK and Nor-X Industry set up a joint objective in 2007 to develop a masterbatch with an optimal composition for the BOPP (biaxially oriented polypropylene) grade (H649FH) of TVK PLC. The main active component of this masterbatch (NOR-Xtm) was iron stearate, which was added to various polymer matrixes (e.g. polypropylene, (PP), or linear low density polyethylene (LLDPE)) to produce masterbatches. These additive masterbatches were then added to the BOPP grade in various

concentrations, and then the films manufactured from the feedstock containing the additives were tested for properties and weather resistance.

Nor-X Industry AS recommended two different masterbatches with PP and LLDPE matrixes for the purposes of the experiments to be performed in 2007. The masterbatches or their 50% mixes were added to the BOPP grade in 1% and 2% concentrations. Then, we checked the colours and qualities primarily of the films extruded from these samples (the error spots (or gels) of cast films are counted by a camera attached to a computer). These two film characteristics are the most critical indicators to decide if the product can meet the property requirements of both processing and application. The following photo shows the films products containing the specific masterbatches. It is conspicuous in the photo that the colour of the masterbatch greatly influences the colour of the finished product. Besides, the number of error spots in each case was higher than specified (Table 2), the elimination of which is a primary objective in our future cooperation.

Samples of cast films were shipped to Nor-X Industry AS where accelerated weather resistance tests were performed on them according to ISO 4892-3. The samples were tested for 1, 3 and 5 days, and others were also aged in a drying oven for 12, 24 and 36 days when their degradation was checked by mechanical tests (the elongation at break and tensile strength of the samples were measured). Figure 6-9. show the results of these measurements. On the one hand, the samples with 2% masterbatch content



Figure 5. LLDPE based film rolls: 1% and 2%; PP based film rolls: 1 and 2%; mixed based film rolls: 1 and 2%

were found to give the best results (containing 2% of either masterbatch, or 2% of the masterbatch mixes). On the other hand, the samples containing the masterbatch had good thermal stability and would not degrade in the oven at a higher rate than the samples containing no masterbatch did. The elongation at break measured in the sample containing 2% of LLDPE base masterbatch would go below 1% in one day, though the same process in the feedstock with PP base masterbatch would not take longer than 3 days, either. Considering these results, we can assume that the samples containing 2% degradation facilitating additive would decompose in 2 or 3 months in the environment.

We can state that UV radiation initiated an expected rate of the degradation process in the samples, which contained the studied additives. However, in the lack of UV radiation (when samples were aged in the oven) the rate of degradation was not found higher than in the reference samples. This means that the degradation process is expected to commence only when the product (packaging material) has been deposited in the environment as a waste and when it is exposed to sunshine. This time, we did not study the cases when the waste is no longer exposed to sunshine after its degradation begins (to see whether the degradation continues or stops).

We are planning to perform a series of tests in the near future where the composition of the masterbatches are further optimised, and intend to involve a wider range of masterbatch concentrations (shifting towards lower concentrations). We believe that these tests can help to prevent the important quality parameters from impairing.

In order to get a more accurate picture of the functions and compositions of these additives, our Company will commence a development project in 2008 with the involvement of the Faculty

Base polymer	Nor-X type	Nor-X content (%)	Average number of gels (<200 μ)	Average number of gels (200-500 μ)	Average number of gels (500-700 μ)	Average number of gels (700-1500 μ)	YI (Yellowness index)
H649FH	-	-	82	0	0	0	-4,08
H649FH	LLDPE base	1	190	3	0	0	0,36
H649FH	LLDPE base	2	211	4	0	0	6,49
H649FH	PP base	1	111	5	0	0	0,15
H649FH	PP base	2	154	3	0	0	3,24
H649FH	mix	1	121	4	0	0	-1,48
H649FH	mix	2	124	5	0	0	0,85
Limit	-	-	100	5	0	0	

Table 2. The results of film qualification (number of error spots of various sizes)

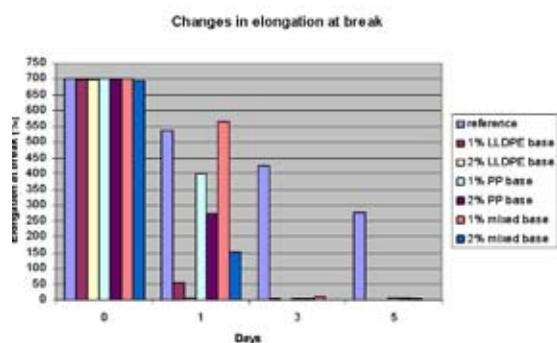


Figure 6. Changes in the elongation at break found in the various samples subjected to weather resistance tests

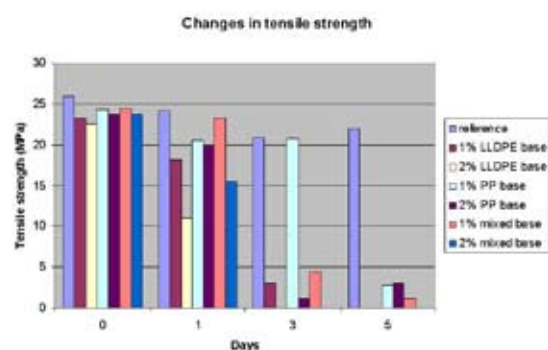


Figure 7. Changes in tensile strength found in various samples subjected to accelerated weather resistance tests

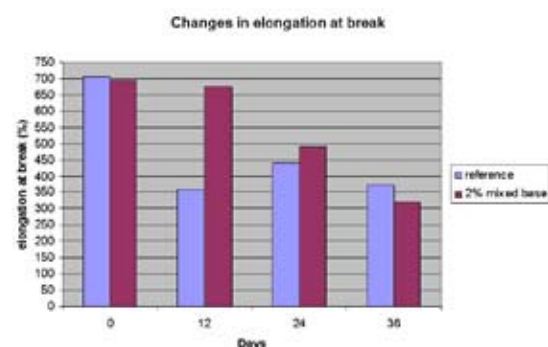


Figure 8. Changes in elongation at break found in the reference samples and in the specimens with 2% mixed masterbatch during their aging in the oven

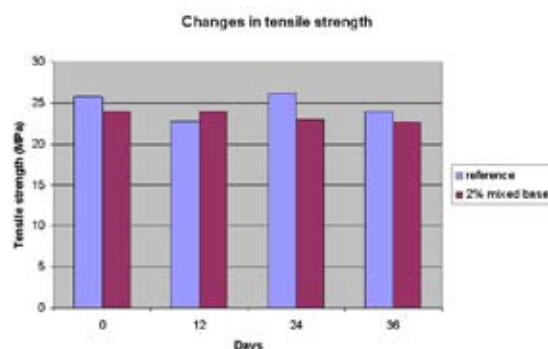


Figure 9. Changes in tensile strength measured in the reference samples and in the specimens containing 2% mixed masterbatch during their aging in the oven

of Organic Chemistry of the Pannon University, which has long experience in organometallic catalytic processes.

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